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Test of the new model for the equation of state of liquids

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The free volume theory of Lennard-Jones and Devonshire has been modified considering the migration of molecules from one cell to another The free energy of the system has been calculated from the principles of statistical mechanics without affecting the main features of the analytical method of Kirkwood. The validity of the model is tested by deducing the equation of state for this model and comparing the calculated and observed values of P^*V^*/NT^* for liquid hydrogen at various isotherms.

Introduction

The liquid state is the least understood of the three common states of matter. Many models have been suggested for explaining the specific properties of liquids. But the free volume model of the liquids with its various modifications has been most widely applied. The basic free volume theory of liquid state has been developed by Lennard-Jones & Devonshire (1937); (referred to as LJD theory hereafter) In this theory all the molecules are assumed to be at their lattice sites excepting the one under observation. This molecule under observation (wanderer) moves in a confined space, a cage or a cell, formed by its neighbours. The volume of this cage is the free volume available for this wanderer. There are three serious drawbacks in the LJD theory. Firstly, it neglects the possibility of migration of molecules from one cell to another Secondly, the connection of this theory with regorous statistical mechanics is obscure (Hill 1956a) Thirdly, the potential used by them is found to be defective (Rossi 1965) and need to be replaced by a deeper and steeper potential. Jansons & Prigogine (1950) and Pople (1951) considered the problem from the principles of statistical mechanics

A modified free volume theory is suggested by Misra (1969, 1970) in which the migration of molecules from one cell to another has been considered. In this model it is assumed that each molecule is confined to a cage (cell) formed by its neighbours, whereas some of the cells are moving in space. Physically, it means that the liquid is practically solid in structure with loose molecules at places. Hence each molecule is having vibratory motion and the loose molecules

may have translatory motion in addition. Thus the migration of molecules from one cell to another has been taken into consideration.

In the present study, it has been shown that the free energy of this system can be calculated following essentially the method of Kirkwood The validity of the model is also tested by deducing the equation of state for this model and comparing the calculated and observed values of P^*V^*/NT^* for liquid hydrogen, for various isotherms.

The probability density $P^{(n)}$ that molecule 1 will be observed in dv_1, 2 in dv_2... and n in dv_n irrespective of the configuration of the remaining $N-n$ molecules is (Hill 1956b)

$$P^{(n)} = \frac{\int_{V'} \dots \int \exp(-\phi/kT) dv_{n+1} \dots dv_N}{Q_N^{(n)}} \quad \dots (1)$$

where $Q_N^{(n)}$ is the configurational integral for the system and V' is the volume of the system diminished by the volume of the n cells occupied by the n molecules.

$$P^{(n)} = \frac{\int_{V'} \dots \int \exp(-\phi/kT) dv_{n+1} \dots dv_N}{\{\int_{\Delta_1} \dots \int_{\Delta_n} \exp(-\phi/kT) \pi^n{}_{i=1} dv_1\} \{\int_{V'} \dots \int \exp(-\phi/kT) \pi^N{}_{i=n+1} dv_i\}}$$

$$= \frac{1}{\int_{\Delta_1} \dots \int_{\Delta_n} \exp(-\phi/kT) \pi^n{}_{i=1} dv_i}$$

$$= \frac{\int_{\Delta_{n+1}} \dots \int_{\Delta_N} \exp(-\phi/kT) \pi^N{}_{i=n+1} dv_i}{Q_N^{(1)}} \quad \dots (2)$$

where $$Q_N^{(1)} = \int_{\Delta_1} \dots \int_{\Delta_N} \exp(-\phi/kT) \pi_{i=1}{}^N dv_i \quad \dots (3)$$

The free volume can be obtained from this distribution function after Hill (1956c) in the form

$$v_f = \int_0^{a-\sigma_0} \exp\left(-\frac{E(r)-E(0)}{kT}\right) 4\pi r^2 dr \quad \dots (4)$$

when $$E(r) = E(0), \; v_f = \tfrac{4}{3}\pi(a-\sigma_0)^3 \quad \dots (5)$$

The free energy can be written in the form (Hill 1956d)

$$A = -N\,kT \ln \frac{v_f \sigma_{(n)}}{\Lambda^3} + \frac{N}{2} E(0) \quad \dots (6)$$

Kirkwood defined a quantity σ^N (Hill 1956e) as

$$\sigma^N = \sum_{m_1 \dots m_N} \frac{1}{\pi_{i=1}^N m_i!} \frac{Q^{(m_1 \cdots m)}{}_N}{Q_N^{(1)}} \quad \dots (7)$$

with the restraint that $\sum_{s=1}^{N} m_s = N$ where N is the total number of molecules in the system. $Q^{(m_1 \ldots m_N)}$ is the configurational integral where m_1 molecules are in cell 1, m_2 molecules are in cell 2, ... and m_N molecules are in cell N. $Q_N^{(1)}$ is the configurational integral when each cell contains one molecule

Hence the configurational integral for the system is

$$Q_N = \sigma^N Q_N^{(1)}. \qquad \ldots \quad (8)$$

It has been suggested (Misra 1969) that a workable theoretical model for the liquid state can be obtained by the assumption that out of N molecules in a system only n molecules are confined to their respective cells, whereas, the rest are capable of migration. The configurational integral for the system can be written as (Naik & Misra 1970)

$$Q_N^{(n)} = \{ \int_{}^{\Delta_1} \ldots \int_{}^{\Delta_n} \exp(-\phi/kT) \pi_{i=1}^{N} \mathrm{d}v_i \} \left\{ \frac{1}{(N-n)!} \sum_{l_{n+1}=n+1}^{N} \ldots \sum_{l_{N-n+1}}^{N} \right.$$

$$\left. \int_{}^{\Delta l_{n+1}} \ldots \int_{}^{\Delta l_N} \exp(-\phi/kT) \pi_{i=n+1}^{N} \mathrm{d}v_i \right\}. \qquad \ldots \quad (9)$$

The first factor in the right hand side of the equation (9) is the contribution of n localised molecules, which are virtually distinguishable, the second factor is that of $N-n$ molecules which are indistinguishable. If $\sigma_{(n)}^N$ is defined as $\frac{Q_N^{(n)}}{Q_N^{(1)}}$, from equation (9)

$$\sigma_{(n)}^n = \frac{\left\{ \frac{1}{(N-n)!} \sum_{l_{n+1}=n+1}^{N} \ldots \sum_{l_{N-n+1}}^{N} \int_{}^{\Delta l_{n+1}} \ldots \int_{}^{\Delta l_N} \exp(-\phi/kT) \pi_{i=n+1}^{N} \mathrm{d}v_i \right\}}{\int_{}^{\Delta_{n+1}} \ldots \int_{}^{\Delta_N} \exp(-\phi/kT) \pi_{i=n+1}^{N} \mathrm{d}v_i} \qquad \ldots \quad (10)$$

This can be further simplified to

$$\sigma_{(n)}^{N\nu} = \frac{(N-n)^{N-n}}{(N-n)!} = \exp(N-n) \text{ by Stirling's approximation.} \qquad \ldots \quad (11)$$

The equation (11) satisfies the two limiting conditions i.e $\sigma_{(n)} = 1$ for high density case and $\sigma_{(n)} = e$ for low density case. The expression of $\sigma_{(n)}$ in equation (11) contains one unknown quantity n, the number of localised molecules, which has been given in the form (Misra 1970)

$$n = N\{1 - \exp[-E(0)/CkT]\} \qquad \ldots \quad (12)$$

The expression for n contains a factor C in the exponent because of the fact that the molecule in the cell is bound to C nearest neighbours. If one bond is broken the molecule escapes from the cell.

The ratio P^*V^*/NT^* has been calculated by Lennard-Jones & Devonshire using Lennard-Jones potential. The calculated numerical values for this ratio becomes greater than its observed values. (Johnston *et al* 1954). The consideration of migration according to the present model increases this discrepancy still further. It may be noted here that any attempt to improve upon the LJD model only worsens the final result. This means that the defect of LJD model is partially balanced by the defect in the Lennard-Jones potential So this potential needs to be replaced by a more suitable potential as suggested by Rossi (1965).

In a previous paper (Misra 1970) a simpler potential was used and a qualitative agreement with the observed values has been obtained in the case of liquid hydrogen. Moreover this potential has been successfully utilized to develop a new theoretical model (Misra 1970, 1969) for explaining many properties of liquids and gases quantitatively. In the present study the same potential is being employed to develop an equation of state and it is seen that the consideration of migration improves the result thus found.

This is a rigid elastic potential in the form

$$\phi(R) = -\mu \exp\left[-\lambda(T^{\frac{1}{3}} - T_m^{\frac{1}{3}})(R-\sigma_0)\right] \qquad \ldots \quad (13)$$

where

$$\mu = \frac{3kT}{2\sqrt{2}\left[\exp\{\lambda\sigma_0(T^{\frac{1}{3}} - T_m^{\frac{1}{3}})\} - 1\right]}.$$

λ and σ_0 are two different parameters of which σ_0 is the effective diameter of the molecules which are assumed to be rigid spheres T is the absolute temperature of the system and T_m is the temperature of the system at which no molecule will have translatory motion. For ordinary liquids T_m is the freezing point. Thus the potential contains two adjustable parmeters λ and σ_0. The minimum for the potential occurs at the wall of the rigid sphere, *i e* when $R = \sigma_0$. This potential is expected to work well in calculating the thermodynamic properties of liquids at moderate temperatures and pressures because here no significant role is being played by short range repulsive part.

The above potential and the corresponding equations can be written in a simple but universal form by introducing molecular units for temperature, volume and pressure. Values of macroscopic quantities expressed in molecular units are given by

$$P^* = \frac{P\sigma_0^3}{\epsilon}, \quad V^* = \frac{V}{\sigma_0^3}, \quad T_m^* = \frac{kT}{\epsilon}$$

where $\epsilon = \frac{k}{(\lambda\sigma_0)^2}$ and k = Boltzmann's constant. So the above potential in equation (1) can be written as

$$\phi(R)^* = -\mu^* \exp\left[-(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})(R^* - 1)\right]$$

$$\mu^* = \frac{3T^*}{2\sqrt{2}\{\exp(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}}) - 1\}} \qquad \ldots \quad (14)$$

POTENTIAL INSIDE THE CELL

Let the system containing N molecules be divided into N cells On the average each cell contains one molecule and there are C nearest neighbours for each molecule. So any molecule under observation is in the field of C neighbouring molecules, the effect of all other molecules may be taken as only 20 percent (Lennard-Jones, 1925) of that of these C molecules. The distribution of potential inside the cell can be calculated in the following way.

Let the C nearest neighbours of a molecule be uniformly smeared over a spherical surface of radius a^* in molecular unit Let the instantaneous positon of the molecule be at a distance of r^* from the centre of the cell, R^* being its distance from a point on the surface of the cell (figure 1) Hence

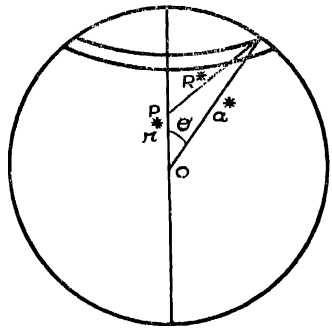

FIGURE 1

$$E^*(r^*) = \frac{C\mu^*}{2a^*r^*(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})^2}\left[\{\exp -(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})(a^* + r^* - 1)\}\{(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})\right.$$

$$\left.(a^* + r^*) + 1\} - \exp\{-(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})(a^* - r^* - 1)\}\{(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})(a^* - r^*) + 1\}\right]$$

$$= -c\mu^* + c\mu^*(T^{*\frac{1}{2}} - T^*m^{\frac{1}{2}})(a^* - 1) + \frac{c\mu^*(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})r^{*2}}{3a^*} + \qquad \ldots \quad (15)$$

The potential when the molecule is at the centre of the cell is given by

$$E(0)^* = -c\mu^* \exp[-(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})(a^* - 1)] \quad \ldots (16)$$

The free volume in equation (5) can also be written in the reduced form as

$$v_f^* = \tfrac{4}{3}\pi\sigma_0^3(a^* - 1) \quad \ldots\ldots (17)$$

Equation of state

From equation (6) the free energy A^* or A/ε can be obtained

$$A^* = -NT^* \ln \frac{v_f^* \sigma_{(n)}}{\Lambda^3} + \frac{N}{2} E(0) \quad \ldots (18)$$

In equation (18) Λ^3 has not been given in the reduced form because it does not appear in the equation of state in the present study. At moderate pressures the volume of the liquid changes slightly and hence λ, a function of specific volume remains approximately constant. So $\frac{\partial \lambda}{\partial v} \simeq 0$ and hence $\frac{\partial T^*}{\partial v^*} = 0$. From equation (18)

$$\frac{P^* V^*}{NT^*} = \frac{a^*}{a^* - 1} - \frac{3c}{4\sqrt{2}} \frac{(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}})}{\{\exp(T^{*\frac{1}{2}} - T_m^{*\frac{1}{2}}) - 1\}} \frac{\partial a^*}{\partial V^*} \cdot V^* + \frac{V^*}{\sigma_{(n)}} \cdot \frac{\partial \sigma_{(n)}}{\partial V^*} \quad \ldots (19)$$

For a face centred cubic lattice a^*, the distance between the centres of nearest neighbour cells is given by $2^{1/6}\left(\frac{V^*}{N}\right)^{1/3}$

To compare the results with observed values for liquid hydrogen the value of σ_0 is taken to be 0.43 as obtained from the best fit by the method of least square, for the specific heat values (Misra, 1969).* The value for σ_0, the diameter of the rigid sphere molecules can be obtained from viscosity data (Misra 1969) since the value of σ_0 is assumed to be the same in the liquid and gaseous states it can be taken as 2.449×10^{-8} cms. (The calculation is not shown here to save space). The results of calculation according to equation (19) are shown in table 1.

In obtaining equation (19) it is assumed that $E(0)^* = E(r)^*$. This means that in the expression for $E(r)^*$ in the equation (15) all other terms excepting the first two are neglected. So terms of the same order from the expression for $E(0)$ have also been neglected as a necessity.

* The qualitative agreement of the calculated values of PV/NKT with observed values for liquid hydrogen has been attempted in a previous paper (Misra 1970).

Table 1. Isotherms for liquid hydrogen

Temperature T^*	Volume in cc/gm mol.	Different terms of P^*V^*/NT^* calculated			P^*V^*/NT^* calculated	P^*V^*/NT^* observed	P^*V^*/NT^* from LJD
		1	2	3			
	25.970	2.6647	2 2927	.0544	.4264	1.0516	1.855
	26.187	2.6526	2.2909	.0548	.4083	.0274	1.834
3.76	26.524	2.6342	2 3087	.0553	.3808	.7568	1.824
	26.921	2.6134	2.3201	0560	3493	1.814	
	27.349	2 5916	2 3322	.0567	3162	3855	1 794
	27.754	2 5718	2 3435	5740	2857	2317	1.784
	26 318	2 6454	2.0183	1733	.8003	1 326	1.879
	27.051	2 6067	2 0367	.1769	7469	1.034	1.882
4 772	28.282	2.5470	2 0668	.1829	.6631	.6528	1.832
	29.774	2 4824	2 1022	1902	.5704	330	1 782
	30 340	2 4598	2 1153	.1930	5375	.324	1 757
	30.988	2 4351	2 1301	.1961	5011	.1408	1 700
	27 587	2 5799	1 7999	2475	1 0275	1.2246	1.86
	28.527	2.5359	1 8199	.2534	.9693	1.014	1.84
5.846	29.720	2 4846	1.8447	.2608	.9007	7857	1.784
	32.323	2 3877	1 8965	.2770	.7682	4638	1.61
	34 027	2 3333	1 9290	.2875	.6918	.339	1.53
	37.774	2 2324	1 9966	3104	.5462	.1985	1.29
	27 887	2.6454	2 0183	.1733	.8003	1 2149	1.874
	29.397	2.6067	2 0367	.1769	.7469	.8968	1.784
6.02	31 134	2 5470	2.0668	1829	.6631	.4654	1.691
	33.090	2.4824	2 1022	.1902	.5704	.4604	1.571
	34 269	2 4598	2 1153	.1930	5375	.3837	1.491
	35.734	2 4351	2 1301	.1961	.5011	.3164	1.411

Note— (1) To consider the effects of the molecules other than the nearest neighbours C, $E(0)$ is increased by 20% as in the LJD theory.

(2) The number of nearest neighbours C is taken to be 8

(3) The results have been calculated by the help of the Computer, at Utkal University, Vani-Vihar.

Discussion

Both Eyring and Lennard-Jones considered σ in equation (11) to be a constant (either 1 or e) So the communal entropy is introduced in the system at one stage. But Rice (1938) suggested that the communal entropy should gradually appear in the system. In the present study it is shown that communal entropy which is given by $NK \ln \sigma + NKT\left(\frac{\partial \ln \sigma}{\partial T}\right)_V$ appears gradually in the system. At the two limits *i.e* solid and dilute gas, the value of this entropy reduces to O & R

The value of P^*V^*/NT^* may be compared with those from the equations of Lennard-Jones & Devonshire (Hirschfielder 1965) It can be clearly seen that the values of P^*V^*/NT^* calculated utilizing Lennard-Jones' potential is always higher than the observed values The results also still worsen with the inclusion of the idea of migration of molecules However the results calculated utilizing the simple potential are in agreement with the experiment to a greater extent It is interesting to see that the calculated results from present study agree quite well for higher temperature at lower volume and vice versa The reason for this is being investigated.

The quantum mechanical calculation of De-Boer & Lunbeck (1948), David & Hamann (1953) Pietrass (1969) have not been discussed here as the only purpose of the present study is to improve upon the original LJD theory The quantum mechanical calculations and the agreement with observed values for other condensed permanent gases will be attempted in subsequent papers.

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